108. *Studies in Polymorphism. Part V. The Linear Rate of Transformation of Monoclinic into Rhombic Sulphur.*

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The linear rate of advance of the interface between β- and α-sulphur has been measured at 20°, 30°, and 40° on polycrystalline films, prepared under controlled conditions, and containing a large proportion of the β-crystals with their *b*(010) faces in the plane of the film, and their direction of elongation (*c* axis) approximately at 90° to the film edge. The rate is constant at constant temperature (in contrast to the behaviour of films of *o*-nitroaniline and mercuric iodide studied in earlier parts of this series), not only in the case of a straight interface started by inoculation of the film edge, but also in the case of nuclei growing in all directions in the plane of the film. The rate increases with the thickness of the film, over the range of thicknesses studied (0·03—0·15 mm.).

The apparent activation energy is 15,000 cals. to the nearest thousand calories, which is considerably less than the internal latent heats of sublimation of the two forms, which are 23,500 (α-) and 22,500 (β-) cals.

Lehmann (" Molekularphysik," Vol. 1, p. 179) studied microscopically the interconversion of rhombic (α-) and monoclinic (β-) sulphur in films prepared by melting sulphur between a slide and a cover-slip. He found that above the transition point (95·6°) the linear rate increases with rise of temperature up to the melting point, whereas below the transition point, the rate first increases with fall of temperature, reaches a maximum and thereafter decreases. He also noted that the rate is markedly dependent on the previous thermal history of the specimen. Gernez (*Compt. rend.*, 1885, **100**, 1343, 1382) measured the linear rate below the transition point (transformation of β- into α-sulphur), in tubes of 1—2 mm. diameter, by direct observation of the rate of movement of the interface, the reaction being started by inoculating the surface of the β-sulphur with a crystal of α-sulphur. He found that the rate is constant at constant temperature, and that for certain conditions of preparation of the β-sulphur, it is a maximum at about 55°. He further studied in some detail the influence of variations in the previous thermal history on the rate, and found that the rate decreased (1) with rise in the temperature at which the β-sulphur crystallised, (2) with rise in the temperature at which the sulphur was melted, and (3) with the length of time it was kept in a state of fusion; and that the rate increased with the length of time for which the β-crystals remained at the temperature at which they grew. It may be noted that the lowest temperature at which Gernez melted his specimens was 129·5°. His results appear to have been based on single observations.

Fraenkel and Goez (*Z. anorg. Chem.*, 1925, **144**, 45) studied the rate of transformation of β- into α-sulphur both dilatometrically (mass rate) and in thin films under the microscope (linear rate), the latter being confined to a few measurements at (presumably) room temperature. They found that if the sulphur were heated above 130° before the experiment, brown S_μ was formed in quantity and both the mass and the linear rates were considerably reduced. They also observed that between room temperature and the transition point, the tendency for nuclei of the α-modification to form spontaneously was negligible, and that the optimum temperature for nucleus formation was — 20°.

The present paper describes measurements of the linear rate of transformation of β- into α-sulphur in polycrystalline films at 20°, 30°, and 40°. It was originally intended to extend the temperature range of study to the transition point, but circumstances have made it necessary to discontinue the work for the present.

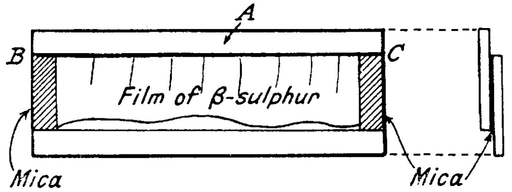
The low tendency to spontaneous nucleation of β-sulphur reported by Fraenkel and Goez (*loc. cit.*) suggested to us that sulphur would be an excellent subject for study on the lines of the work already described in Parts III and IV (J., 1935, 1860; 1938, 1636), since it meant that (1) the reaction could be started at will by inoculation after the substance had had time to acquire the thermostat temperature, thus avoiding the necessity for extrapolating to zero time (see Parts III and IV, *locc. cit.*), and (2) it would be easy to establish a rectilinear interface which would greatly simplify the method of measurement. It was realised that these advantages might be offset by the molecular complexity of sulphur and the resulting sensitiveness of its behaviour to variations in its previous thermal history. In the event, however, the expected advantages have been fully realised, and by the careful avoidance of overheating and by control of the conditions of crystallisation, complications due to the presence of unstable molecular species have, it is believed, been reduced to a minimum.

EXPERIMENTAL.

Purification of Material.—" Pure crystalline " sulphur (Messrs. Hopkin and Williams) was recrystallised once from redistilled carbon disulphide, the first crystals to be deposited being rejected, and was dried in a vacuum desiccator for one week. The sulphur was then placed in a glass tube sealed at one end, and connected at the other by means of a rubber stopper to a tap leading through a calcium chloride tube to a filter-pump. The sulphur was melted by heating the tube to a temperature not exceeding 123°, and the tube evacuated by means of the filter-pump. Occluded gases and residual traces of carbon disulphide were thus removed. The sulphur was allowed to solidify, and dry air admitted to the tube, which, when cold, was coarsely crushed in an agate mortar. The lumps of sulphur were picked out with a platinum spatula and transferred to weighing bottles, which were stored in a desiccator over calcium chloride.

Apparatus.—The apparatus was essentially similar to Apparatus 1 used for *o*-nitroaniline (Part III, *loc. cit.*) but differed from it as regards (*a*) the slides, (*b*) the slide holder, and (*c*) the screen.

FIG. 1.

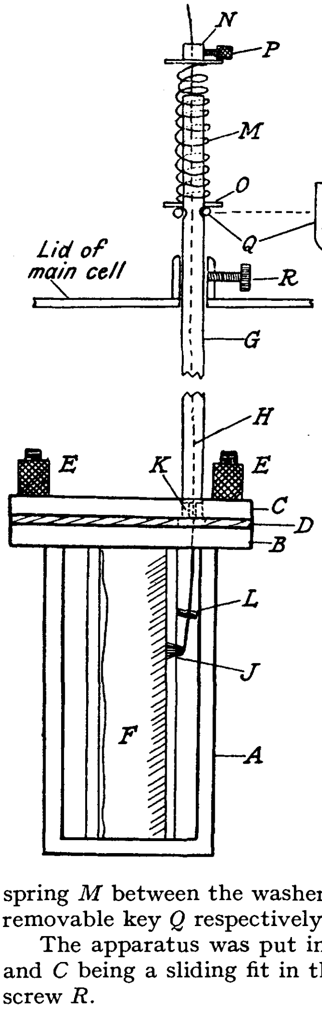


The sulphur films were confined between 3″ × 1″ slides separated from one another by cleavage strips of mica and sealed thereto with phenol–formaldehyde cement (see Part IV) applied in the form of an acetone solution. The slides were first cleaned, steamed, and baked as described in earlier parts of this series, and their thickness measured at many different points by means of a micrometer screw gauge, those showing variations greater than 0·02 mm. being rejected. During measurement the slides were stood on edge in a groove in a brass block, thus avoiding handling. A number of the slide and mica cells (see Fig. 1) were then built up (all manipulation being done with forceps) and these were piled alternately with thin strips of brass, placed across the ends of the slides, in a screw press by means of which a gentle pressure was applied to the glass–cement–mica junctions. Press and cells were then baked in an oven to harden the cement. The purpose of the brass strips was to prevent the cells becoming stuck together by excess cement forced out in the early stages of the baking, when the cement is very fluid.

After the sulphur film had been introduced into a cell (see below), its average thickness was determined by measuring the thickness of the cell at many different points, and subtracting the average thicknesses of the slides. Since the films were much thicker (0·06—0·10 mm.) than those used in previous studies (0·01—0·02 mm.), their percentage variations in thickness due to unevenness of the glass surfaces were much less. It was possible to use these thicker films because of the low nucleation tendency of β-sulphur.

The films were prepared as follows. The cell (Fig. 1) was laid on a hot plate, and the temperature raised to 123°; it was not allowed to exceed this value, in order to avoid as far as possible the formation of molecular species unstable at lower temperatures. By means of a platinum spatula a lump of the purified sulphur was placed on the lower slide at *A*, where it projected beyond the upper one, and on melting, the sulphur was drawn in between the slides by capillary action. More sulphur was added if necessary until the space between the slides was full, and any excess sulphur on the step *A* was cleaned off with the spatula. The cell was then transferred to another hot plate at 100°, and 10 secs. after the transfer, crystallisation of β-sulphur was induced by drawing a platinum wire, trimmed to a chisel point, along the edge *BC*. Elongated crystals grew inwards from this edge, and owing to contraction, the opposite edge of the film was drawn in to some extent, as shown in the figure. The above conditions were found by trial to give films best suited to the velocity measurements. If crystallisation was induced sooner than 10 secs. after transfer to the second hot plate, large β-crystals giving a ragged interface were produced; if later, the crystals were small and tended to be opaque.

Fig. 2.



The slide holder is shown in Fig. 2. It differed from the slide holders used in Parts III and IV in being air-tight and in incorporating an inoculating device. It was thought desirable to make it air-tight, because it seemed possible that the fall of velocity observed in our previous studies on *o*-nitroaniline and mercuric iodide might have been partly due to loss of material from the interface by evaporation.

A was a brass box, $3\frac{1}{8}''$ × $1\frac{15}{16}''$ × $\frac{5}{16}''$, with large glass windows back and front, sealed on with white vacuum wax. The top of the box consisted of a thick brass flange *B*, the upper surface of which was ground flat. The lid of the box, *C*, was a thick brass plate, the under surface of which was ground flat and covered with the rubber sheet *D*. By means of the milled heads and bolts *E*, lid and box could be firmly bolted together, forming an air-tight joint. The cell *F* containing the film of β-sulphur occupied the position shown, being held against the near window by leaf springs (not shown). The inoculating device consisted of the brass tube *G* screwed and sweated into the lid *C*, and containing a length of piano wire *H*, bent in a smooth curve as shown, and having a small stiff brush *J* fixed at its lower end. This brush was formed of a flat bundle of test-tube brush bristles bound together with fine wire and soldered to *H*; before the experiment, it had been dipped in a solution of sulphur in carbon disulphide and allowed to dry, so that the bristles were thus coated with rhombic sulphur. By manipulating the end of *H* projecting above *G*, the brush could be caused to travel from one end to the other of the edge of the film of β-sulphur (*BC* in Fig. 1), thus initiating the transformation with a rectilinear interface. The movement of the brush was guided by the step on the film cell, and by the piano wire passing through the small hole in the brass plug *K*, fixed in the lower end of *G*. *K* was ground off flush with the under surface of *C*. When not in use, the brush was drawn up to the top of *A* so that the rubber-faced brass washer *L* which was soldered to *H* was pressed against the underside of *K*, a circular opening having been left in the rubber sheet *D* to allow of this. The holder was then completely sealed. The brush was held in this position by the compression of the spring *M* between the washers *N* and *O*, which were fixed in position by the screw *P* and the removable key *Q* respectively.

The apparatus was put inside the main cell in the thermostat [Part III, Fig. 1 (*a*), *E*], *B* and *C* being a sliding fit in this cell, and it was fixed in position at any desired height by the screw *R*.

The screen was a sheet of plywood suitably supported and stiffened, on which was fixed a sheet of white cardboard ruled vertically with parallel lines in Indian ink. This was held to the plywood by horizontal cork-lined strips of wood running across the top and bottom, and clamped to the plywood with bolts and wing nuts. The position of the cardboard could thus be easily adjusted. The screen was at a distance of 16 ft. from the projection lens of the apparatus, and the magnification obtained was × 27. The distance between the lines on the cardboard was 27 × 0·25 mm., *i.e.*, it corresponded to a distance of 0·25 mm. on the actual film.

Method of carrying out an Experiment.—The position of the cardboard screen was adjusted so that the first line was coincident with the image of the film edge *BC* (Fig. 1). After time had been allowed for the film to acquire the temperature of the thermostat, this edge was inoculated, and any slight shift of the film cell resulting from this operation was remedied by a further adjustment of the screen. The α-modification appeared in a finely divided form, almost opaque to light, and so the position of the interface was very sharply defined. The time required to reach thermostat temperature varied from 25 to 45 minutes, depending on the temperature, and had been found previously by a method similar to that described in Part IV.

The interface was usually almost exactly a straight line up to the first 0·25 mm. of its travel, but thereafter developed a more or less irregular contour. The first method used to time the reaction was simply to estimate the mean times taken for the interface to reach the successive lines on the screen, by taking the means of the respective times at which the most forward point and the most backward point on the interface reached each line. Any abnormal promontories or indentations were ignored, and if an appreciable section of the interface was as a whole more advanced or more retarded than the rest, it was timed separately. A number of films were measured in this way by one of us (P. G. E.) until, on taking the results in the order in which they were obtained and dividing them into two halves, the average velocity calculated from the first half agreed to within a few units % with that calculated from the second half. This was taken to indicate that sufficient measurements had been made to yield a characteristic value. These measurements were confined to 20° and 30°, and the results corresponded to an apparent activation energy of 13,600 cals.

There was a very large personal factor involved in this method, owing to the responsibility laid on the experimenter of deciding what sections of the interface were " abnormal," and this was demonstrated when the work was taken over by another of us (J. E. D. J.), who was unable to repeat the results already obtained at 30°. The method had the further objection that, since comparatively great lengths of the interface were timed as a whole, the degree of approximation of the " mean time " as defined above to the true mean time of crossing a line depended very much on the contour of the interface. It was therefore abandoned for the more trustworthy statistical method described below. It is noteworthy, however, that although the absolute values of the average velocities obtained by the two methods differed appreciably (in the ratio of about 2 : 3), the results for the apparent activation energy agreed to within 2000 cals.

The statistical method consisted in ruling the screen into 20 horizontal sections, each of width equivalent to 1·5 mm. on the actual film, and noting the mean time required for the interface to advance across the intervals of 0·25 mm. defined by the vertical lines in each section. The mean times were then plotted on a distribution curve and treated by statistical methods. The interface movement was followed for a distance of 1·5 mm., so that the total number of mean time readings obtained from each film, it being assumed that no part of the interface was ignored, was $(1{\cdot}5/0{\cdot}25) \times 20 = 120$. It should be explained that this treatment of the time values together, irrespective of the distance from the film edge to which they referred, was possible because the rate was found to be linear in agreement with the observations of Gernez (*loc. cit.*). The method of timing was to inspect the screen every 2 mins. at 20° and 30° and every minute at 40°, and note in which sections the interface had just reached a vertical line or was on the point of having completely passed over it. Eventually this resulted in a record of two times for every 0·25 mm. of advance in every section, one time being that at which the most forward point of the interface had reached the line, and the other that at which it had just all passed over, accurate to within 2 mins. at 20° and 30°, and 1 min. at 40°. The mean of these two times was taken as the mean time of crossing. Since the sections were so short, abrupt changes in the contour of the interface were given much more nearly their correct weight in the final analysis than in the first method, where they were liable to exert a wholly disproportionate influence. The personal factor was almost entirely eliminated in the second method, since no part of the interface was ignored except for some quite unequivocal reason such as incomplete inoculation.

The projection lamp was only switched on when the screen was being inspected, and previous experiments with thermocouples had shown that illumination of the film at the intervals given above and for the few seconds needed to carry out the inspection did not appreciably raise its temperature.

Study of Nuclear Growth.—Films which had only been melted once did not nucleate spontaneously (cf. Fraenkel and Goez, *loc. cit.*) except on very rare occasions. Films that had been remelted, however, usually developed a few isolated nuclei in the interior, and these nuclei grew as roughly circular patches. The growth of a number of these was measured at 20° by tracing their outline on the screen at intervals of about one hour, and determining the average linear rate of advance of the interface from the tracings as follows. If the tracing was a completely closed area, it was measured with a planimeter and the interface advance taken as the radius of a circle of equal area. If not, the planimeter–rotameter method used for mercuric iodide (Part IV) was applied.

Since the spontaneous nucleation of the remelted films indicated that remelting had caused some change in the system, they were not used for the studies of growth induced by inoculation of the film edge, which formed the main part of the work.

DISCUSSION OF RESULTS.

At an early stage in the work it became apparent that, as found by Gernez (*loc. cit.*), the linear rate of advance of the interface obtained by nucleation of the film edge is constant at constant temperature, at least up to a distance of 1·5 mm., which was the limit of our measurements in most cases. This is in sharp contrast to the decline of velocity observed with *o*-nitroaniline and mercuric iodide, and is not to be explained on the basis of a small difference of density between α- and β-sulphur, as the following calculation shows. Mercuric iodide, which shows a strong decline within the first 1·5 mm. of advance, has *d* 6·322 (red) and 6·092 (yellow). The ratio of the corresponding linear dimensions of compact polycrystalline blocks of equal weight of the red and the yellow form is therefore $(6{\cdot}092/6{\cdot}322)^{\frac{1}{3}} = 0{\cdot}988$. The corresponding ratio for sulphur is $(1{\cdot}938/2{\cdot}036)^{\frac{1}{3}} = 0{\cdot}984$, if one uses the densities calculated from the *X*-ray measurements of Warren and Burwell (*J. Chem. Physics*, 1935, **3**, 6) and Burwell (*Z. Krist.*, 1938, **98**, 123). Hence, the shrinkage on transformation should be slightly the greater in the case of sulphur. A possible explanation of the absence of a fall of velocity is that the crystals in the sulphur films show a decidedly preferred orientation (see later) with regard both to the plane of the film and to its edge, and that the transformation in crystals having this orientation involves shrinkage in directions other than those in the plane of the film. Hence, no gap is formed and no hindrance to the advance of the interface develops.

FIG. 3.

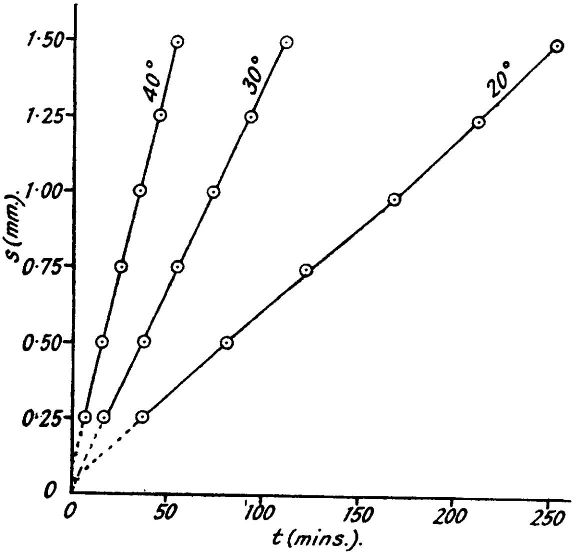


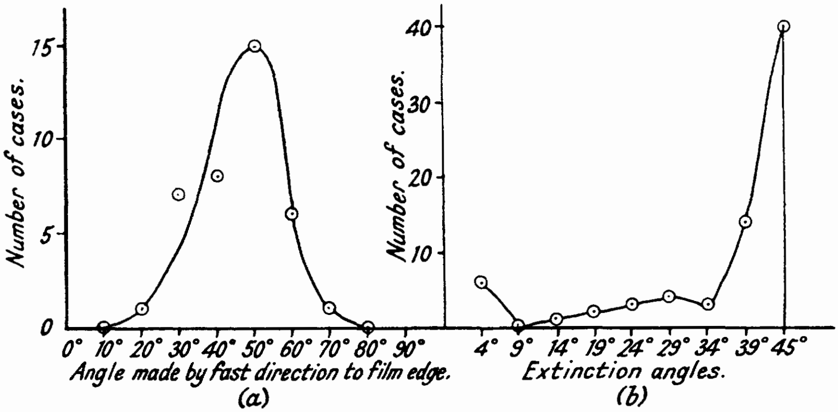
Table I and Fig. 3 give the average time (*t*)–distance (*s*) relationships. The points lie very nearly on straight lines which extrapolate to the origin at 30°, and to slightly above it at 20° and 40°. The latter deviations are probably due to the conditions being somewhat abnormal near the edge of the film, for it was observed microscopically that here the crystals were somewhat smaller than those farther in, and it was also possible that the film was slightly thicker owing to roughness at the edge of the glass (thicker films show higher rates; see later). Further, the inoculating brush probably penetrated some little way beyond the edge in places, and gave the interface an " unfair " start.

TABLE I.

Average time (t)*-distance* (s) *results.*

	t (mins.) at					
s (mm.).	20°.	Δ*t*.	30°.	Δ*t*.	40°.	Δ*t*.
0·25	37·0		17·3		6·9	
		44·1		20·4		8·8
0·50	81·1		37·7		15·7	
		40·2		16·8		9·1
0·75	121·3		54·5		24·8	
		43·7		18·4		9·6
1·00	165·0		72·9		34·4	
		45·5		19·6		10·1
1·25	210·5		92·5		44·5	
		42·7		18·4		8·9
1·50	253·2		110·9		53·4	

FIG. 4.



The numbers on the abscissæ give the upper limit to the group. For instance, in (a), 50° *means* 41—50°; *in* (b) *the last group contains* 6 *values,* viz., 40—45°.

A systematic examination of the first 1·5 mm. of a typical film of β-sulphur under the polarising microscope showed it to consist of long tabular crystals, many showing signs of having been formed by a dendritic type of growth, interspersed with material which was too finely divided or too confused to be resolved. Most of the tabular crystals showed extinction angles of about 45° with reference to their axis of elongation, and this axis was at or near 90° to the edge of the film. Groth (" Chemische Kristallographie ") gives 44° as the maximum extinction angle of β-sulphur, so that these crystals may be identified as lying on the *b*(010) face. The " fast " and " slow " directions were determined by means of cleavage flakes of gypsum (the crystals were too thick for the ordinary compensators to be of any use), and Fig. 4(*a*) shows the distribution of angles (in groups of 10°) made by the fast direction to the film edge for 38 crystals having extinction angles of 40—45°. Fig. 4(*b*) shows the distribution of extinction angles (in groups of 5°) among 73 crystals. In addition, 10 crystals were observed which gave no, or only a faint, extinction and were therefore optic axial sections (indices *h*0*l*, from Groth's description). Fig. 4(*b*) indicates three favoured positions corresponding to extinction angles of 0—4°, 25—29°, and 40—45°, the last predominating, as stated above. The first two of these positions are probably determined by other faces parallel to the *c* axis, in which case the first would be determined by the *a*(100) face.

In Fig. 5 are shown the curves (unbroken lines) giving the distribution of the times, determined as described in the " Experimental " part, required for the interface to advance 0·25 mm. The first measurements for which this method was used were done at 30° on 13 films, involving the taking of some 1500 time readings, and as can be seen from the figure, an almost smooth distribution curve was obtained. A similar number of time readings were therefore taken at 20° and 40°. The curves are all similar in being slightly skew towards the lower time values, and there is doubtless a connexion between this and the distribution of crystal orientations. The time values, expressed in minutes, were collected into groups of 4 at 20°, 2 at 30°, and were plotted without grouping at 40°. The figures given on the abscissæ are the averages for each group at 20° and 30° ; for instance, the figure 39·5, the value for the peak (mode) of the curve at 20°, is the mean of the group 38, 39, 40, 41.

The position of the mode on the time axis was fixed by calculating Pearson's coefficient of skewness. The broken curves are normal distribution curves fitted around the mean value and enclosing the same area as the experimental curves. These curves were constructed by standard statistical methods. The standard deviations between the experimental and the normal curves are : at 20°, 0·46 ; at 30°, 0·48 ; at 40°, 0·40 ; and these show a reasonably close agreement. It is therefore evident that the peaks of either the experimental or the normal curves may be taken as characteristic of the linear rate at the different temperatures under the conditions of preparation of the films, film thickness, and crystal orientation already specified, and afford a satisfactory basis for computing the apparent activation energy. Fig. 6 shows the result of plotting the logarithms of the rates based on the experimental peaks (modes), the normal peaks (means), and the slopes of the *s–t* graphs in Fig. 3, and the relevant data are collected in Table II. The corresponding activation energies are 15,500, 15,150, and 14,500 cals. respectively, of which the first two may be taken as the more trustworthy.

FIG. 5.

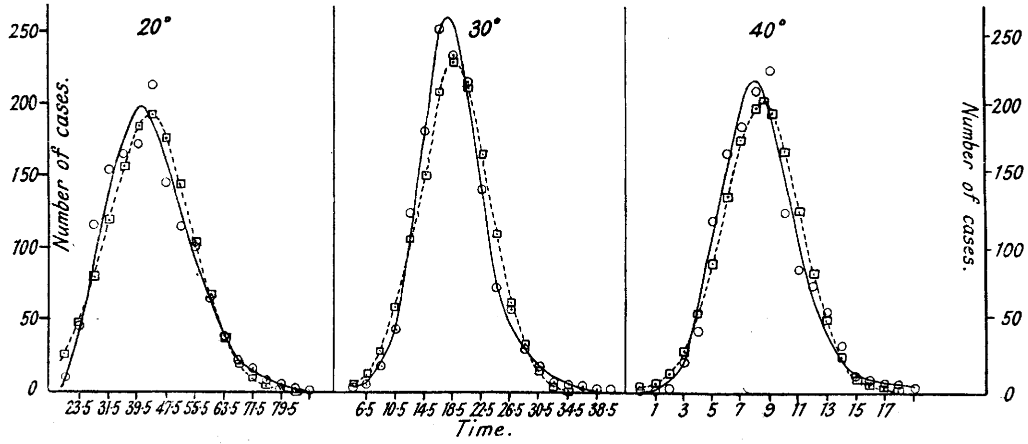


TABLE II.

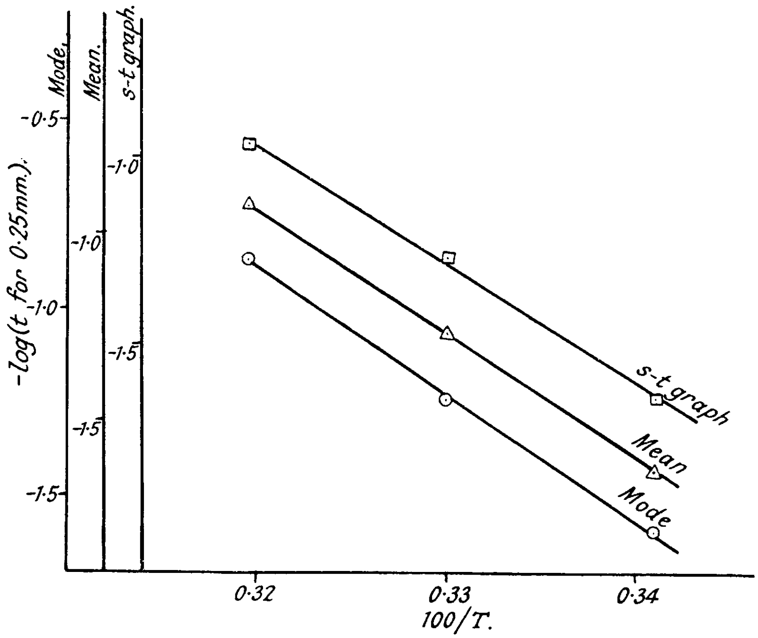
Times (mins.) for an interface advance of 0·25 *mm.*

	20°.	30°.	40°.	*E* (cals.).
Mode	39·5	17·5	7·5	15,500
Mean	43·5	18·5	8·5	15,150
s–t graphs	44	18·5	9·25	14,500

The internal latent heats of sublimation of α- and β-sulphur calculated from the vapour-pressure measurements of Neumann (*Z. physikal. Chem.*, 1934, **171**, 416) are 23,500 and 22,500 cals. respectively. A calculation of the apparent activation energy over the range 20—30° on the assumption that molecules must acquire the heat of sublimation in order to move from one lattice to the other has been made by the method given in Part IV (p. 1644), and the result is about 22,000 cals. This figure is derived from scalar properties of the substance, whereas the experimental value of the apparent activation energy has a largely vectorial basis, owing to the preferred crystal orientation shown by the films. A direct comparison between these figures cannot therefore be made, but their difference is so large that, unless the activation energy or the heat of sublimation varies widely from face to face, it may be concluded that, as was found in the case of mercuric iodide, a molecule needs less activation energy for the transformation than that which it must acquire to escape completely from either lattice.

Effect of Film Thickness.—The films used for the above experiments had average thicknesses ranging from 0·06 to 0·10 mm. Thinner films would have shown large percentage variations in thickness owing to the unevenness of the glass slides, and thicker films were not so easy to study as they stopped a good deal of light and gave a dull image on the screen. Some experiments were made with thinner (0·03—0·05 mm.) and with thicker (0·12—0·15 mm.) films, and these showed that the average rate increases with film thickness, the rate for the thicker films being about 1½ times that for the thinner ones.

FIG. 6.



Nuclear Growth.—The growth of 26 nuclei in remelted slides was studied mainly with the object of finding out whether they would exhibit a fall of velocity. As already indicated, the advance of the interface obtained by inoculation of the film edge proceeds very largely along the length direction of the β-crystals, whereas the growth of a nucleus in the interior of the film proceeds in all directions in the plane of the film, and might cause the formation of cracks and a slowing up of the reaction in certain of these directions. The rate proved, however, to be constant and of the same order as that of growth from the film edge. It would appear therefore that the shrinkage must be confined, at least mainly, to directions other than those in the plane of the film, unless perhaps cracks develop in the α-form *after* the interface has passed, and not at the interface. Certainly the opacity of the α-form indicates that it is extensively broken up. Further work is obviously needed to settle this point.

Our thanks are due to Professor S. Sugden, F.R.S., for the fruitful suggestion that statistical methods could be applied with advantage to this work, to Professor A. R. Richardson for much helpful advice and discussion regarding the details of applying these methods, and to Mr. H. R. Hopkin for carrying out the statistical calculations.

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